STRUCTURE AND CRYSTALLIZATION SPECIFICS OF ALUMINA-BEARING LANTHANIDE BOROGERMANATE GLASS

V. N. Sigaev,[1] E. V. Orlova,[1] S. V. Lotarev,[1] and E. V. Lopatina[1]

The paper investigates the structure and crystallization specifics of glass behaving as a precursor of a pyroelectric material with a unique combination of properties of the composition $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ depending on the quantity of Al_2O_3 additive. It is established that as the alumina content grows, the crystallization of glass essentially changes: the propensity of glass to oriented surface crystallization of ferroelectric $LaBGeO_5$ is suppressed and the share of lanthanum borate and germanate grows. The type of crystallization of glass correlates with IR spectroscopy data, indicating that modifications of the glass structure caused by increasing Al_2O_3 content lead to substantial changes in the $BO_3 : BO_4$ ratio.

The physicochemical and crystallization properties of lanthanum-borogermanate (LBG) glasses [1 – 5] give reason to attribute them to promising polar glass-ceramic dielectrics. The volume and surface crystallization of ferroelectric crystals $LaBGeO_5$ with the stillwellite-type structure provides for the development of surface and volume structure with nonlinear properties (optical, ferroelectric, pyroelectric, piezoelectric, etc.). The formation of $LaBGeO_5$ crystals in glass volume is considered by the authors of [1] as a model process of the formation of a nonlinear optical nano- and microcomposite medium. The formation of $LaBGeO_5$ crystals from LBG glasses at temperatures close to the vitrification temperature t_g was observed in [4 – 6]. At higher temperatures LBG glasses have clearly expressed oriented surface crystallization [2], which can lead to the formation of perfect textures. The LBG system has been used to produce nearly perfect textures of needle-shaped crystals of ferroelectric $LaBGeO_5$ with high pyroelectric activity [3] and also transparent surface layers of $LaBGeO_5$ crystals with nonlinear optical properties [4].

The texture-forming capacity of different glass systems depends on many factors: glass compositions taking into account losses of component in volatilization, content of impurities, melting and cooling conditions, thermal conditions of crystallization etc., which had not been earlier investigated in detail [2, 6]. Therefore, the reproducibility of microstructure and physical properties of textured glass ceramics, including the LBG system, remains rather low. The correlation between a glass composition and its texture-forming capacity is very complicated, which is well illustrated by the authors in

[6] who observed the texture formation of ferroelectric $Pb_5Ge_3O_{11}$ in glasses of the $PbO – GeO_2$ system within a very narrow composition range. When a composition deviated from the optimal one within $\pm 0.3\%$, texture formation was almost totally suppressed. For other systems, data on the dependence of texture formation on the basic glass composition and additives introduced are missing.

Knowledge of the specified factors is a necessary condition for controlled oriented crystallization of glasses allowing for forming polyfunctional textured materials [3, 4, 7].

In our study we compare the structure and crystallization of LBG glasses of the stillwellite stoichiometric composition $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ with Al_2O_3 additives in an amount of 0, 1, 2, 3, 5, and 7% (R, R1, R2, R3, R5, and R7, respectively, here and elsewhere wt.%) that were melted in platinum crucibles and glass melted in a corundum crucible (glass A).

Glass samples weighing 50 g of composition $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ with Al_2O_3 additives were obtained by melting batches in platinum or corundum crucibles at 1300°C for 30 min, which corresponds to the method in [2]. To obtain glass of a prescribed composition, we took into account the volatilization of B_2O_3 by weighing the mixture and the crucible before and after melting.

The differential thermal analysis (DTA) of glasses was performed on solid and powder samples using Al_2O_3 as the reference standard.

The x-ray phase analysis (XPA) of initial and crystallized glasses was performed on a DRON-3M diffractometer on powder samples and the texture-forming capacity of glasses was estimated on plate-shaped samples.

---

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

The structure of glasses was analyzed by IR spectroscopy in the range of $4000 - 400$ cm^{-1} (a Nicolet system equipped with a DTGS sensor (KBr)). The spectral resolution was 2 cm^{-1}. The samples of analyzed glass powder in the amount of 4 mg were mixed in an agate mortar with KBr and then molded as plates of weight 200 mg.

The microstructure of crystallized glasses was studied on a BS-311 electron scanning microscope by depositing a thin gold film on the fracture surface of samples.

The melts of glasses R, R1 – R3 were partly crystallized in cooling in a crucible or when poured on a metal plate without molding. The crystallization capacity of glasses rapidly decreases, as alumina content grows: glasses R5, R7, and A did not contain any crystalline inclusions under the same melting and cooling condition, whereas pure glasses R, R1 – R3 were obtained by pressing a melt sample poured on a metal plate to a thickness of $1 - 2$ mm. The strong dependence of crystallization capacity of LBG glasses on Al_2O_3 content is presumably related to the precise correspondence of the composition P to the stoichiometry of stillwellite due to correcting the batch for boron volatilization.

The DTA curves of hardened LBG glasses in their solid and powder forms are shown in Fig. 1. Both curves in Fig. 1a clearly exhibit typical deviations from the basic line in the vitrification range, which makes it possible to determine t_g corresponding to the inflection point. The t_g values of glasses R and A are 672 and 679°C, respectively. The slightly increased t_g of glass A could be caused by the presence of a certain quantity of alumina dissolved in glass. At higher temperatures the DTA curves differ significantly: we see a sharp exothermic crystallization peak and a blurred exothermic effect within a wide temperature range in glasses R and A, respectively.

The values t_g on DTA curves of powder samples (Fig. 1b) grow smoothly with increasing alumina content (the temperatures of vitrification and the exothermic peak maximum for the DTA curves shown in Fig. 1a and b of glass $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ with Al_2O_3 additives are listed in Table 1); t_g of solid and powder glasses R and A agree well. At the same time, as Al_2O_3 content increases, the exothermic peak gradually decreases and becomes blurred, yet the exothermic peaks on the DTA curves of glasses R7 and A look almost identical. Consequently, the variations of t_g and the exothermic behavior of the considered glasses depends on Al_2O_3 content.

To identify the crystal phases formed at the temperature of the exothermic effect registered on the DTA curves (Fig. 1), glass samples R and A were heated at a rate of 10 K/min to the temperature of the exothermic effect termination for glass R (950°C) and then cooled to room temperature. The diffraction patterns of the samples are shown in Fig. 2. The stillwellite-type $LaBGeO_5$ is the only phase formed in glass R. Glass A is insignificantly crystallized and contains binary phases of lanthanum pyrogermanate
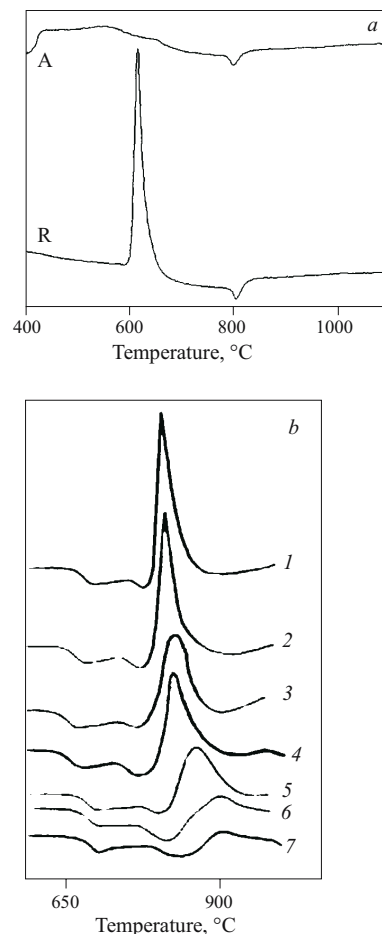

Fig. 1. DTA curves: a) solid glass samples R and A (air medium, heating rate 10 K/min, DSK Netsch 404 instrument, sample weight 50 mg); b) glass powders R (1), R1 (2), R2 (3), R3 (4), R5 (5), R7 (6), and A (7) (air medium, heating rate 10 K/min, Paulik – Paulik – Erday derivatograph, sample weight 0.5 g).

$La_2Ge_2O_7$ (JSPDS 23-213) and lanthanum borate $BaBO_3$ (JSPDS 13-571) and small quantities of stillwellite.

To compare the crystallization of initial glasses at temperatures approaching the exothermic peak, polished plates of thickness 0.5 mm were prepared from these glasses. After

TABLE 1

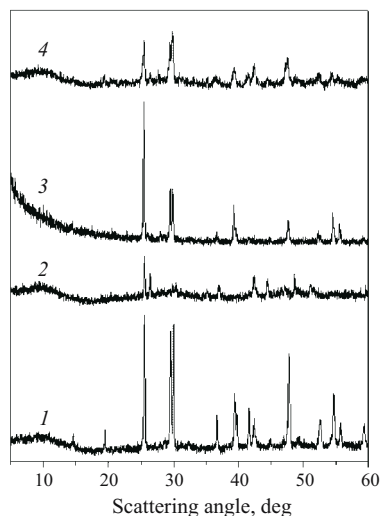| Glass	Weight content of Al_2O_3, %	Crucible material	Temperature, °C	
			vitrification	exothermic peak maximum
R	0	Platinum	670 (672)[*]	820
R1	1	"	667	820
R2	2	"	672	830
R3	3	"	673	830
R5	5	"	676	870
R7	7	"	679	900
A	–	Corundum	682 (679)[*]	920

[*] According to data in Fig. 1a.

Fig. 2. X-ray patterns of glass powders R (*1*, *3*) and A (*2*, *4*) heat-treated under following conditions: heating at a rate of 10 K/min to 950°C and exposure 10 min (*1*, *2*); exposure at 950°C for 4 h (*3*, *4*).
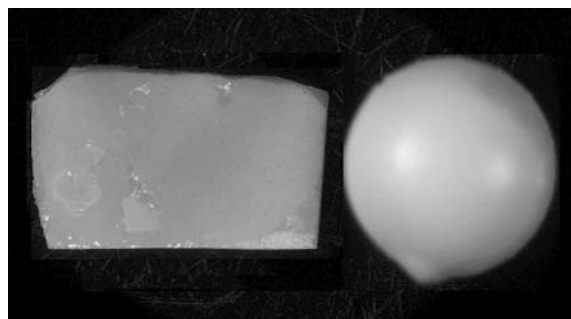

Fig. 3. Photos of plates R and A heat-treated at 950°C for 4 h (× 20). The glass A plate has acquired a ball shape.

Fig. 4. Electron microphotos of a plate of glass R: surface texture to a depth of 50 – 70 μm (*a*) and volume texture (*b*).

2 h heat treatment, plates of glass A due to their softening acquired a spheroid shape, whereas glass R crystallized with the formation of textured glass ceramics without perceptible deformation of the plates (Fig. 3). The surface of the plates of compositions R2 – R5, R7 was partly fused under thermal treatment at the same temperatures; the higher the alumina content, the higher the fusion degree, ranging from slight fusion of the edges (composition R2) to the formation of balls (R7 and A). The electron microscope photos of glass R heat-treated at 950°C corroborate the existence of a volume texture (Fig. 4) and the x-ray pattern in Fig. 5 identifies it as highly ordered $LaBGeO_5$ texture.

The IR spectra of glasses R and A (Fig. 6) have wide bands typical of glass, which corroborates the amorphous structure of the samples. For reference purposes, in Fig. 6 we also show the UR spectrum of stillwellite-type $LaBGeO_5$. The structure of $LaBGeO_5$ described in [8] is based on tetrahedron $[BO_4]$ chains extending along axis 3_1 and related to germanium 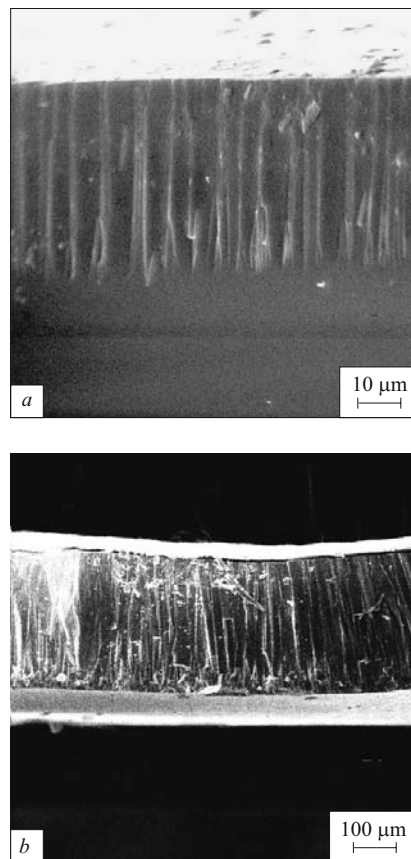tetrahedrons so that each tetrahedron $[GeO_4]$ is linked by its vertexes with two $[BO_4]$ tetrahedrons of the same chain and with two lanthanum polyhedrons. Considering the data on the structure and IR spectra of stillwellite [9, 10] it is not difficult to identify the main bands in the IR spectrum of the La $BGeO_5$ crystal. The main bands in the range of 900 – 1200 cm^{-1} can be attributed to the stretching vibrations of the tetrahedron $[BO_4]$: B – O (B) — 986 cm^{-1} and B – O (Ge) — 926 cm^{-1}. Two bands at 788 and 731 cm^{-1} are generated by the stretching vibrations of the $[GeO_4]$ tetrahedron of the Ge – O (B) and Ge – O (La) types, respectively [9]. The low-intensity bands near 1400 cm^{-1} are presumably related to the presence of residual glass in the sample.

A marked peculiarity of the IR spectra of glasses R and A is the presence of two intense overlapping bands in the range of 1500 – 1200 cm^{-1} due to the stretching vibrations of B – O in $[BO_3]$ triangles [9, 10]. These bands are significantly less intense in the glass R spectrum, but their presence is beyond question. This result, to some extent, is unexpected, since the considered glasses have the stillwellite composition in which boron atoms take only the tetrahedral positions. However, the coexistence of three- and four-coordination boron atoms in LBG glass of composition R was recently corroborated by nuclear magnetic resonance [1, 5].
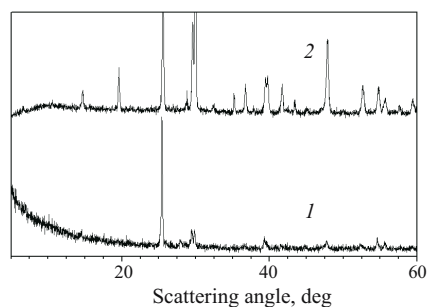
Fig. 5. X-ray pattern of the surface of glass R plate crystallized as texture based on stillwellite $LaBGeO_5$ (*1*) compared to x-ray pattern of the same sample milled to powder (*2*).

Fig. 6. IR spectra of glasses R (*1*), A (*2*), and crystalline $LaBGeO_5$ (*3*).

The band near 1000 cm^{-1} related to the stretching vibrations in tetrahedrons $[BO_4]$ in glass A is vanishingly small, whereas the same band is multiply more intense in the spectrum of glass R (Fig. 6). The bands at 1200 – 1400 and 1000 cm^{-1} indicating the presence of both triangles $[BO_3]$ and tetrahedrons $[BO_4]$ in glass were also observed in silicate glasses of the stillwellite composition $LaBSiO_5$ [11].

The band near 800 cm^{-1} in glasses R and A can be attributed to the stretching vibrations of Ge – O in tetrahedrons $[GeO_4]$ [9]. The bands at lower wave numbers are determined by deformation vibrations.

Since glasses R and A were obtained in the same conditions, except for the crucible material, the differences in their glass structure, crystallization, and texture formation may be related to the presence of a certain quantity of Al_2O_3 in glass A as a result of the corundum crucible dissolution. The data in Fig. 1. fully corroborate this hypothesis. Based on the similarity of the DTA curves of glasses A and R7, it can be assumed that the content of Al_2O_3 in glass A is approximately 7%.

Lately the authors in [12] determined quantitatively the content of Al_2O_3 in various lanthanide borate glasses melted in a corundum crucible. The content of Al_2O_3 in all glasses synthesized at temperatures ranging from 1200 to 1400°C did not exceed 4% and was equal to about 2% for the glass $25La_2O_3 \cdot 75B_2O_3$ melted at 1300°C [12]. The LBG glass melted at 1300 in a corundum crucible contains a significantly higher (triple) quantity of alumina. This discrepancy is possibly related to a significantly larger volume and, consequently, a larger ratio of the volume to the contact surface area of melting lanthanide borate glass with the crucible; however, information on the volume of melted glass in [12] is absent.

It is necessary to stress that, according to the data in [12], crystallization of melt with 8 – 10% Al_2O_3 in lanthanum-borate glass occurs during melt cooling; furthermore, small aluminum concentrations do not affect glass formation. We have observed the opposite effect of alumina on the glass-forming capacity and crystallization behavior of LBG glasses: an abrupt suppression of the crystallization tendency and im-
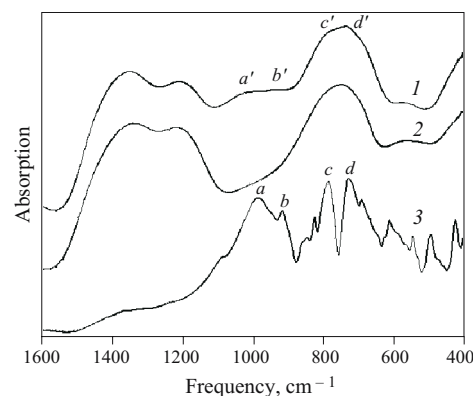
proved glass-forming capacity as the content of Al_2O_3 increased. For LBG glasses this seems quite natural, since alumina caused a deviation of the glass composition from the stoichiometric composition $LaBGeO_5$.

In interpreting IR spectra (Fig. 6) the attribution of bands to vibrations of particular structural units is usually achieved by comparing the vibration spectrum of glass to that of a crystal of similar composition with a similar position and relative intensity of bands [13]. This method is based on the hypothesis assuming that the short-range order in glass and in the respective crystal is identical. Since the far-range order in glass is absent, wide blurred bands arise in the glass spectrum which constitutes the envelope of the crystal spectrum. Such a situation frequently occurs in homogenous glasses whose compositions are close to the stoichiometric crystal composition and outside the phase boundary range [14].

In contrast to the stillwellite crystal spectrum, the spectra of glasses R and A have intense absorption bands in the high-frequency range (Fig. 6) indicating the presence of three-coordination boron atoms. It is known that the coordination numbers of boron atoms in borate, borosilicate, and borogermanate glasses are equal to 3 or 4 [9], whereas triangles $[BO_3]$ and tetrahedrons $[BO_4]$ may construct different superstructural units [15]. In the range of 1500 – 1100 cm^{-1} there are two absorption bands related to stretching vibrations in triangles $[BO_3]$ in the frequency range of 1360 – 1320 cm^{-1} for boroxol rings and 1240 – 1210 cm^{-1} for non-ring fragments of the borate lattice, whereas the band at 1025 – 950 cm^{-1} is determined by stretching vibrations in tetrahedrons $[BO_4]$.

The presence of triangular units $[BO_3]$ in LBG glasses proved by the authors of [1, 5] and corroborated by the data in Fig. 6 determines the discrepancy between the glass structure and the stillwellite structure, in which all boron atoms are four-coordinated. The spectra of glasses and crystals of similar compositions frequently resemble each other regarding the positions of the main absorption bands, allowing for perceptible blurring of bands in the glass spectra. If a glass is homogeneous, the distribution of its main structural units re-

sembles that of the corresponding crystal. If the IR spectrum of a glass perceptibly differs from the crystal spectrum, that suggests the existence of segregation phenomena in glass. In the case of LBG glasses, the high-frequency bands indicate the segregation of atoms.

Thus, it follows from Fig. 6 that glasses R and A contain three-coordination boron atoms in different quantities. The band at 1000 cm^{-1} in glass A related to the vibrations in tetrahedrons [BO_4] is significantly less intense and smaller than the respective band in the glass R spectrum. This indicates an essentially higher concentration of [BO_4] structural units in glass R1, and the low intensity in the range of 1240 – 1210 cm^{-1} points to an insignificant concentration of triangles [BO_3].

The structural information obtained from the IR spectra correlates well with the crystallization behavior of LBG glasses. It is known that during nonisothermic devitrification a crystalline phase emerges in glass with a maximum nucleation and growth rate; in some systems the growth of a metastable phase has been registered instead of a thermodynamically stable phase. It can be stated that during nonisothermic devitrification the formation and growth of a crystalline phase is preferable for kinetic reasons, regardless of its thermal stability. Usually a crystalline phase having a maximum resemblance to the vitreous matrix has the maximum nucleation rate; therefore, its formation is kinetically preferable.

Stillwellite crystals, despite the presence of homogenous nucleation in LBG glasses [4 – 6], grow predominantly from the surface into the depth of the glass, which is a necessary condition for implementing oriented crystallization. It is naturally believed that volume nucleation is the antagonist of texture formation. Therefore, to facilitate texture formation, it is necessary to create conditions facilitating the growth only of the polar phase from the glass surface. In glass R it is only stillwellite $LaBGeO_5$ that grows from the surface as the sample is heated at the rate of 10 K/min, whereas in glass A binary phases are the first to slowly form. Next, at higher temperatures (about 950°C) a stillwellite-like phase is formed in glass A due to secondary recrystallization; therefore, texture formation is largely impeded. According to the data in [4], a thin layer of needle-shaped crystals $LaBGeO_5$ oriented along the axis c may be formed in glass A. However, at subsequent stage of crystallization in glass A volume texturing is nearly absent due to the presence of binary phase crystals in the glass volume. The authors in [1] using the nuclear magnetic resonance method established that the quantity of three- and four-coordination boron in glass R is approximately equal. During crystallization, boron atoms gradually pass to the tetrahedral positions. It is quite probable that a significant decrease in the content of four-coordination boron in the initial glass A corroborated by the data in Fig. 6 hampers the crystallization of the stillwellite-like phase and leads to the loss of the texture-forming capacity.

Indeed, upon heating glass R, stillwellite crystallizes as the first and only phase. It can be assumed that this is related

to a higher content of [BO_4] tetrahedrons in such glass, which facilitates the nucleation of the stillwellite phase. This makes it possible to obtain a high-quality texture extended from one surface of a sample 0.5 mm thick to its opposite surface without a perceptible effect of dendrite growth (Fig. 4). The high degree of orientation of crystals in the texture is confirmed by x-ray phase analysis (Fig. 5).

The presence of alumina in glass A increases the number of [BO_3] polyhedrons, whereas tetrahedrally coordinated boron almost totally disappears. This modification of the glass structure determines an easier formation of binary phase nuclei than that of stillwellite, therefore, stillwellite is not formed as the first crystalline phase when glass is heated.

The good agreement between IR spectroscopy, DTA, x-ray phase analysis, and mass crystallization data makes it possible to identify a correlation between the specifics of the short-range order in LBG glasses and their crystallization behavior. Aluminum oxide additives in LBG glasses cause the transition of tetrahedrally coordinated boron atoms into [BO_3] triangles, which fundamentally modifies the type of glass crystallization. LBG glasses not containing Al_2O_3 experience stable oriented crystallization, which consistently disappears as the content of alumina increases.

REFERENCES

1. P. Gupta, H. Jain, D. B. Williams, et al., "Structural evolution of $LaBGeO_5$ transparent ferroelectric nano-composites," *J. Non-Cryst. Solids*, **349**, 291 – 298 (2004).

2. V. N. Sigaev, P. D. Sarkisov, E. V. Lopatina, and S. Yu. Stefanovich, "Polar glass-ceramic textures based on stillwellite crystals," *Kristallografiya*, **43**, 499 (1988).

3. V. N. Sigaev, "Structure of oxide glasses and formation of polar glass-ceramic textures," *Fiz. Khim. Stekla*, **24**(4), 295 – 307 (1998).

4. Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, "Second harmonic generation in transparent surface crystallized glasses with stillwellite-type $LaBGeO_5$," *J. Appl. Phys.*, **89**(10), 5282 – 5287 (2001).

5. H. Jain, "Transparent ferroelectric glass ceramics," *Ferroelectrics*, **306**, 111 – 127 (2004).

6. S. Shimanuki, S. Hashimoto, and K. Inomata, "Oriented grain growth from lead germanate glasses," *Ferroelectrics*, **51**, 53 – 58 (1983).

7. Y. Ding, Y. Miura, S. Nakaoka, and T. Nanba, "Oriented surface crystallization of lithium niobate on glass and second harmonic generation," *J. Non-Cryst. Solids*, 259, 132 – 138 (1999).

8. A. A. Voronkov and Yu. A. P'yatenko, "X-ray study of atomic structure of stillwellite $CeBO[SiO_4]$," *Kristallografiya*, **12**, 258 – 262 (1967).

9. E. I. Kamitsos, A. Patsis, M. A. Karakassides, and G. D. Chryssikos, "Infrared reflectance spectra of lithium borate glasses," *J. Non-Cryst. Solids*, **126**, 52 – 67 (1990).

10. A. Rulmont and P. Tarte, "Lanthanide borogermanates $LnBGeO_5$: synthesis and structural study by x-ray diffractometry and vi-

brational spectroscopy," *J. Solid State Chem.*, **75**, 244 – 250 (1988).

11. I. Kratochvilova-Hruba, I. Gregora, J. Pokorny, et al., "Vibrational spectroscopy of LaBSiO$_5$ glass and glass-crystal composites," *J. Non-Cryst. Solids*, **290**(2 – 3), 224 – 230 (2001).

12. N. N. Vinogradova, L. N. Dmitryuk, and O. B. Petrova, "Vitrification and crystallization of glasses based on borates of rare-earth elements," *Fiz. Khim. Stekla*, **30**(1), 3 – 8 (2004).

13. H. Verweij, J. H. J. M. Buster, "The structure of lithium; sodium and potassium germanate glasses studied by Raman scattering," *J. Non-Cryst. Solids*, **34**, 81 – 99 (1979).

14. N. Sigaev, I. Gregora, Pernice, et al., "Structure of lead germanate glasses by Raman spectroscopy," *J. Non-Cryst. Solids*, **279**, 136 – 144 (2001).

15. A. C. Wright, N. M. Vedishcheva, and B. A. Shakhmatkin, "The interrelationship between the structures of borate glasses and crystals," in: *Borate Glasses, Crystals & Melts*, The Society of Glass Technology, Sheffield (1997), pp. 80 – 87.